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THE EFFECT OF HYGROSCOPICITY ON THE SENSITIVITY OF EXPLOSIVES AND IGNITERS

THEODORE M. GILLILAND

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ON THE SENSITIVITY OF EXPLOSIVES AND IGNITERS

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Theodore M. Gilliland

THE EFFECT OF HYGROSCOPICITY ON SENSITIVITY OF EXPLOSIVES AND IGNITERS

By

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Lieutenant Commander, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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Thesis

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ABSTRACT

The amount of moisture adsorbed by lead ozide, lead styphnate, black powder, and an ignition mixture containing zirconium, under isothermal conditions, was determined by weight during this investigation. The relative humidity was varied from 25% to 100% while maintaining a constant temperature of 82 deg. F. within a range of plus or minus two degrees. A comparison was then made of the sensitivity of the moist explosives and igniters with that determined for a dry sample. Lead azide was compared on the basis of impact sensitivity, the others on the basis of thermal sensitivity. The objective of the experiment was to measure quantitatively the hygroscopicity of the substances and to determine the effect of the moisture adsorbed on their thermal or impact sensitivity..

The writer wishes to express his appreciation to Professor James E. Sinclair of the U. S. Naval Postgraduate School for assistance, advice and encouragement during the course of this project. A word of thanks is also extended to Dr. R. A. Reinhardt, Professor J. W. Wilson, LCDR. J. L. Carter, LT. R. L. Rhodes, LT. O. C. Chisum, LT. V. L. Harris, and to the members of section OP-2 for advice, assistance and suggestions.

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TABLE OF SYMBOLS

Symbol	Quantity
x	Grams of moisture adsorbed
m	Weight of the dry sample in grams
y	Percentage of moisture adsorbed, x/m times 100
Ps	Partial pressure of the water vapor in mm Hg
P	Total pressure in mm Hg
k	Constant for Freundlich and Patrick Equations
n	Exponential constant for Freundlich and Patrick Equations
z	Receiprocal of n
a	First constant for the Langmuir Equation
b	Second constant for the Langmuir Equation
gamma	Surface tension

INTRODUCTION

Hygroscopic effect is one of the many physical properties of explosives and igniters. Unlike impact sensitivity, detonation velocity, temperature of detonation or ignition, and relative power, very little information is available on the hygroscopicity of explosives or on the effect of moisture on their explosive properties. The word "hygroscopic" is defined in Webster's Dictionary as "readily absorbing and retaining moisture", and "sensitivity to moisture". This investigation deals with this property of lead azide ($Pb(N_3)_2$), lead styphnate, or by its chemical name, lead 2, 4, 6 trinitro-resorcinate ($C_6 H(NO_2)_3O_2Pb$), black powder (KNO_3, charcoal, and sulfur), and a zirconium ignition mixture of which the exact composition is not known.

These explosives and igniters were chosen for testing because of the key position they usually occupy in an explosive or ignition train. Lead styphnate is the most common compound used where detonation is to be instigated by thermal means, while lead azide occupies a similar position when impact initiation is contemplated. Black power and, more recently, metallic ignition mixtures are used as the igniters to start the burning of solid rocket propellant grains. These compounds usually represent the first step in effecting the desired detonation or ignition.

Explosives are noted for the unpredictable manner in which they sometimes act. There are many instances in which explosions have occurred for unknown reasons, and many in which they have failed to react at the time or in the manner desired. It is possible that some of these failures could be attributed to exposure to moisture prior to being installed. On the other hand, if the hygroscopic effect is negligible, the need for controlled atmospheres could be dispensed with. In either case a knowledge of the effect of moist atmospheres is of interest to persons dealing with explosives.

There are many variables affecting the amount of moisture which will be adsorbed by solid substances. These include temperature, pressure, partial pressure of water vapor, the particle size of the solid, surface area exposed, the porosity of the substance, and its chemical nature. The hygroscopic sensitivity could be a phenomenon involving only the surface of the solid and in this case would be referred to as adsorption. The surface could be only partially covered by water molecules, it could be completely covered by a film of one molecular thickness, or there could be more than one layer of thickness. This would depend, among other things, upon the unsaturated forces on the surface of the crystalline lattice of the substance. For the isothermal process, the equations of Freundlich and Langmuir would apply (1).

Freundlich Equation: $$y = k(p_s)^z$$

Langmuir Equation: $$y = \frac{a b p_s}{1 + a p_s}$$

See page v for explanation of symbols. If the molecules of the gaseous phase penetrated among the molecules of the solid phase more or less uniformly, the phenomenon would be one of absorption. According to the "Capillary Condensation Theory" of Zsigmondy (1) some substances, in addition to being covered with a monomolecular film of water, have the vapor being condensed to a liquid in the pores of the substance. This condensation is caused by a lowering of the vapor pressure due to surface tension effects. Patrick (1) enlarged on this theory and proposed that the adsorption of porous substances was due entirely to capillary condensation and was independent of the chemical nature of the substance.

Patrick Equation: $$y = k\left(\frac{p\gamma}{p_s}\right)^z$$

The following exerpt concerning experimentation with nitro-cellulose seems pertinent:

> "As the equilibrium shifts toward saturation, there is added to chemical fixation, a physical absorption and capillary condensation which depends upon the amount of surface and porosity. These properties vary within the same sample when beaten or gelatinized." (2)

It is difficult to decide whether to call phenomenon of this type absorption or adsorption. McBain suggested that it would be more appropriate to term it persorption because of the effect of the pores of the adsorbent.

An attempt was made to eliminate all variables except the partial pressure of the water vapor, and to measure the effect of varying this property. The same batch of each explosive and igniter was used throughout to minimize the effect of particle size and composition differences. The sample sizes were limited to one-half of a gram and spread in a thin layer to approximate the same surface area per unit weight on successive runs. The variation of atmospheric pressure was considered to be negligible in comparison with the uniformity to which the temperature could be maintained. Adsorption decreases with increasing temperature and increases with increasing pressure. It is interesting to note that a refrigeration cycle was devised employing this principle (3). No attempt was made to determine quantitatively the effect of increased temperature on hygroscopicity. The rapid increase of the partial pressure of water vapor with increasing temperature would be offset to some extent by the decreased adsorption due to the increased mobility of the molecules with increasing temperature.

Impact sensitivities were determined on a two kilogram impact machine designed by James E. Sinclair, and the method described in his report (4) was used. Thermal sensitivities were determined on a spark gap apparatus. The statistical 50% point of explosion or ignition was used as the basis for determining the effect of moisture by a comparison of this point for moist and dry samples.

APPARATUS

The most effective equipment for preparation of the samples turned out to be the simplest. All the items needed, with the exception of the Constant Temperature Air Bath, were available in the Explosives Laboratory. The equipment used during the project was as follows, the figure and item to the right identifies articles shown in photographs:

Constant Temperature Air Bath	Fig. 2
Analytical Balance	
Chemicals for Constant Humidity	Fig. 7
Desiccators, 200mm	Fig. 1, Item 1
Jars, wide mouth with top	Fig. 1, Item 2
Weighing Funnels	Fig. 1, Item 3
Aluminum Cups	Fig. 1, Item 5
Watch Glasses, small	Fig. 1, Item 6
Impact Machine	Fig. 6
Spark Gap Apparatus	Fig. 3
Wet Meter, flow	
Gas Washing Bottles, Fisher-Milligan	Fig. 1, Item 8

Two general methods of exposing the samples to moist air were tried. The first method consisted of passing air at a low flow rate through a series of gas washing bottles containing a sulfuric acid or saturated salt solution to regulate the relative humidity, thence through a fiber glass and an asbestos filter to prevent carry-over, through the powder in the bottom of a U tube (Fig. 1, Item 7), and finally through a flow meter where the volume of flow was recorded. This method was satisfactory as to results but presented several disadvantages. The change from one relative humidity to another involved the use of large amounts of chemicals and was time consuming. The weight of the U tube was excessively large compared to the weight of the powder sample it contained because of the necessity of including a ground glass filter in the downstream side of the tube to prevent the loss of a portion of the sample. Weighings were slow with respect to the time elapsed from removal from the apparatus, weighing and returning to the apparatus. It was also difficult to remove

the sample from the tube for testing and to clean the tube in preparation for another run. The second method consisted of placing the sulfuric acid or saturated salt solution in the bottom of an air tight vessel with the sample in a separate small container on a pedestal inside the vessel. The first system tried in this method consisted of having the sulfuric acid or saturated salt solution in the bottom of a desiccator with the samples in weighing funnels, on watch glasses, or in aluminum cups on the porcelain plate of the desiccator. This method was advantageous in that eight samples could be run at the same time. Its disadvantage was in the bulk of the desiccators, and in the fact that once the lid was removed to weigh one of the samples the equilibrium conditions within the vessel were disturbed and the remaining samples were probably affected. In place of the desiccators, the use of wide mouthed jars about three inches in diameter and three inches high (Fig. 1) was adopted. The jars were of sufficient size to hold one sample in an aluminum cup on a glass pedestal over the saturated salt solution in the bottom of the jar. The cap was of a type which permitted sealing of the jar when the sample was in place. By using 15 jars, it was possible to conduct runs on three different compounds at the same time. The jars with their samples could be placed beside the balance or the test apparatus and kept closed until the instant when the weighing or testing was to be done.

As was mentioned above, three types of containers for exposing the explosives and igniters were tried. Of these, the aluminum cups were the best. Small watch glasses, due to their shape, made it very difficult to prevent loss of some of the sample during handling. Weighing funnels were excellent for handling but their limited surface area made it difficult to spread the powders out in a thin even layer. The aluminum cups had high sides which prevented loss of a portion of the sample, had a large, flat, smooth surface on which to spread out the powders, and were disposable.

Constant humidity can be achieved either by the use of a sulfuric acid or a saturated salt solution in water. Both methods were used

during the course of this project. Values of relative humidity for various salt solutions at various temperatures were obtained from the International Critical Tables (5). Sufficient data were available to permit plotting or extrapolation to obtain the relative humidity at the temperature being used. A plot of relative humidity versus temperature for the salts used is shown in Figure 9. In addition to being easier to prepare, the salt solution remained constant with long periods of usage whereas the sulfuric acid solution changed as moisture was adsorbed by the sample and lost to the atmosphere when the vessel was opened.

The combination of the jars with the saturated salt solution and the aluminum cups were the most satisfactory with respect to speed, convenience and accuracy and were used to prepare the samples. Desiccators were used to store prepared samples at a desired relative humidity when testing was to be done at a later time and the jars were required for the preparation of new samples.

A constant temperature air bath, Figure 2, was constructed of Cello-Tex. It was approximately two feet square at the ends and four feet long. Temperature was regulated by means of a thermostat controlling two 100 watt light bulbs which served as the heating element. Air circulation was provided within the box by means of a small fan. A plot of the temperature in the box was maintained on a 24 hour temperature recorder to insure that the temperature had remained within the prescribed limits during a run.

A picture of the spark gap apparatus is shown in Figure 3 and a schematic wiring diagram in Figure 4. With 110 volts and 1.36 amperes impressed on the primary coil, a potential of 3,000 volts existed on the squib which contained the sample being tested. A variac on the power supply made possible settings from zero to 130 volts. When the firing key was closed, the spark passed through the sample between the pins and the casing of the squib. The details of the squib are shown in Figure 5. The impact machine used for testing lead azide is shown in Fig. 6 and described in reference (4).

Fig. 1. Equipment Used During the Project
1. Desiccator, 2. Jar, 3. Weighing Funnel, 4. Squib, 5. Aluminum Cup, 6. Watch Glass, 7. U Tube, 8. Gas Washing Bottle

Fig. 2. Constant Temperature Box

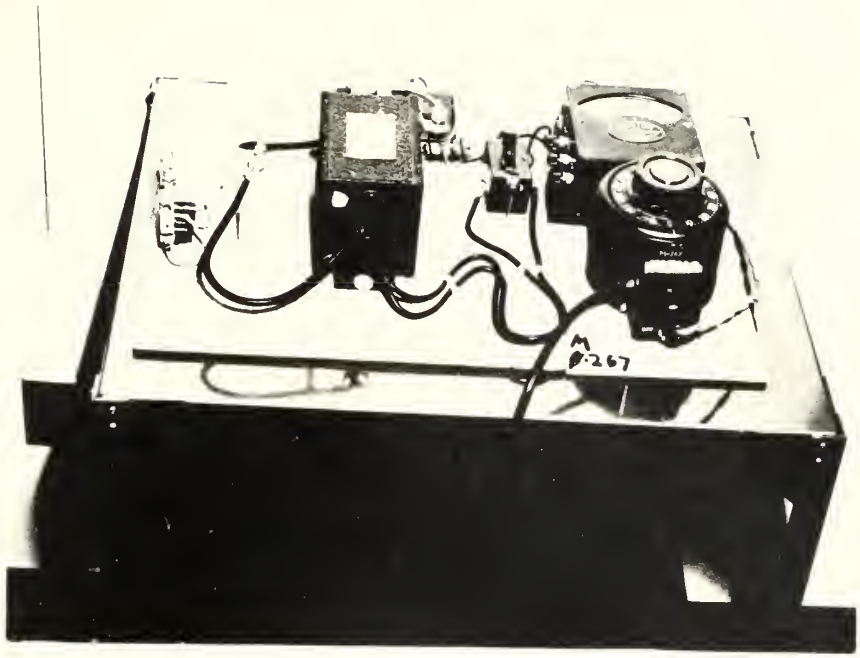


Fig. 3. Spark Gap Apparatus

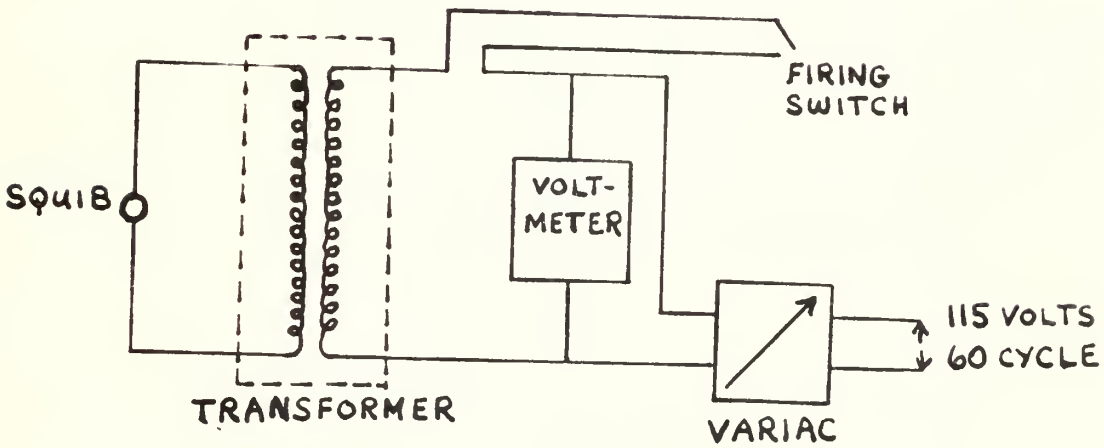


Fig. 4. Schematic of the Spark Gap Apparatus

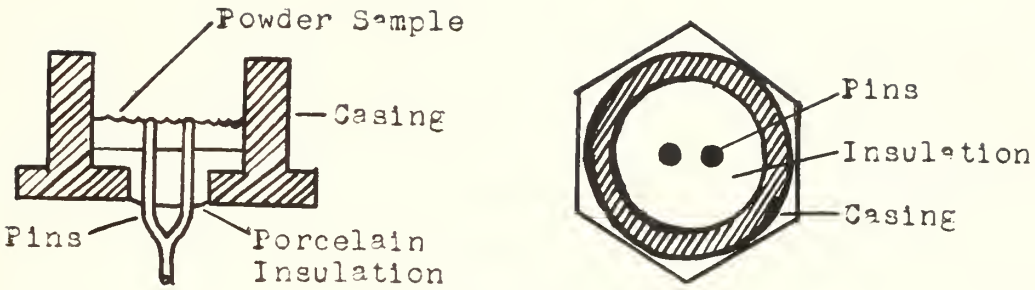


Fig. 5. Details of the Squib

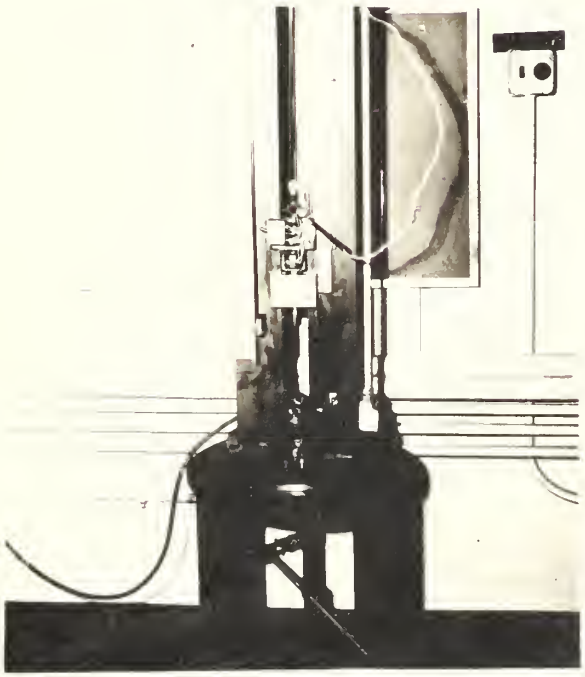


Fig. 6. The Impact Machine

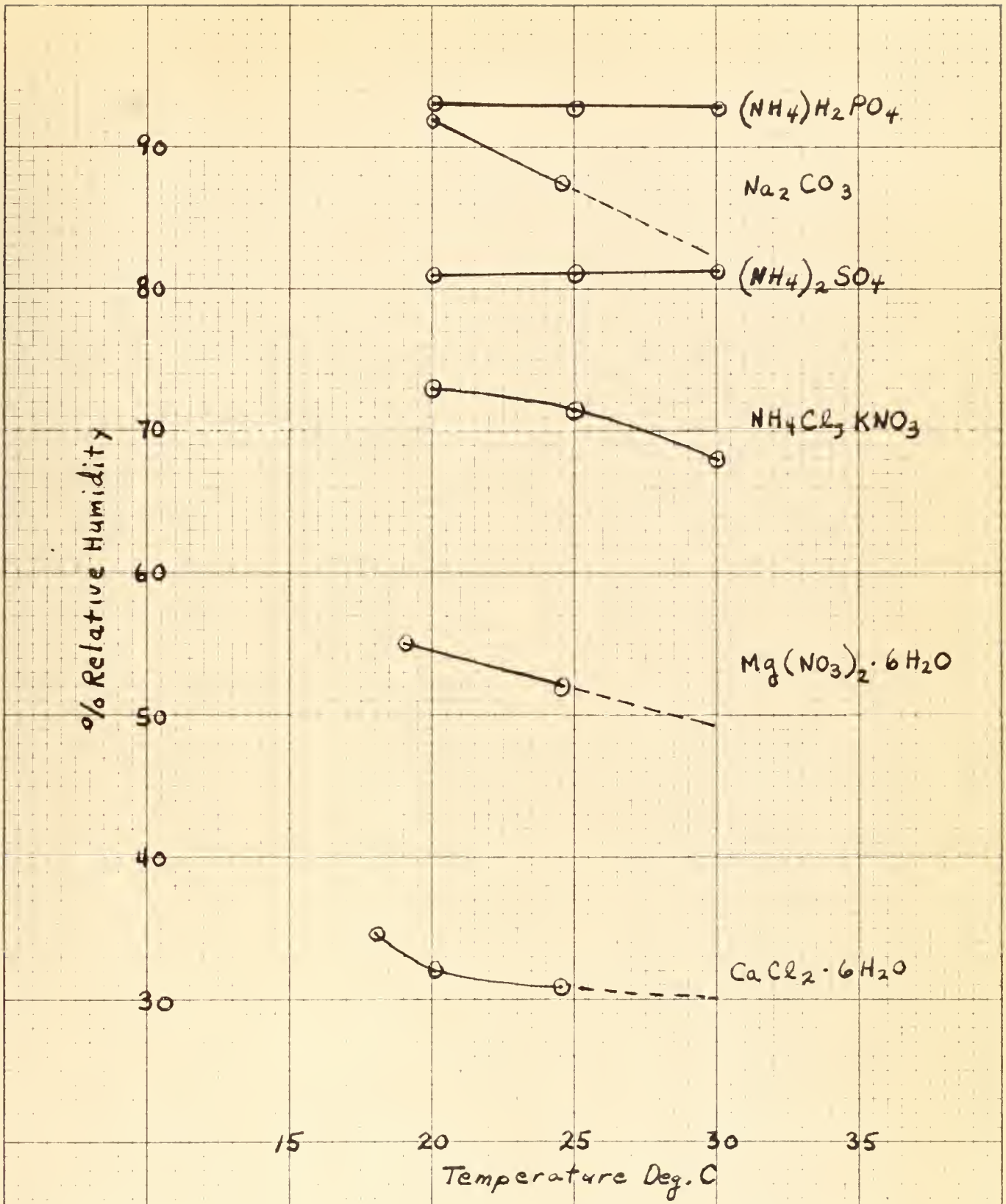


Fig. 7. % Relative Humidity vs Temp. Deg. C.
(For Salts Indicated when in Saturated Solution)

EXPERIMENTAL PROCEDURE

1. Preparation of the Samples.

The explosives and igniters being investigated were spread in thin layers in a container and placed in a vacuum oven at 160 deg. F. for a period in excess of 48 hours for drying. On completion of this period, they were cooled in a desiccator containing activated alumina powder and then weighed. This procedure was repeated to insure that all moisture and volatiles had been removed. This procedure was adequate for drying all of the substances except the lead styphanate. A period of over three days was used in this case. Lead styphnate which had been exposed to moisture was extremely difficult to dry. Placing it under ethanol for 24 hours and then drying in the vacuum oven for over three days insured dryness. After the initial drying, the powders were dept under a desiccant and then dried in the oven for 24 hours just prior to being used. As was previously mentioned, the same lot of each compound was used throughout to insure the same average particle size.

The containers to be used were placed in their jars to reach equilibrium with their intended atmosphere before being weighed. The container was then weighed on the analytical balance to the nearest milligram and loaded with the sample from a desiccator near the balance. The powder was spread in as thin and even a layer as possible in the container and the weight was then determined to the nearest one tenth of a milligram. This weight was used as the basis from which to determine the amount of moixture adsorbed by noting the increase of subsequent weighings. This gave an accuracy of three significant figures in both the weight of the powder sample and the weight of the moisture adsorbed. The percentage of moisture adsorbed, x/m times 100, was then rounded off to two significant figures. The sample was then sealed in a jar at a regulated humidity, the time recorded, and the jar placed in the constant temperature bath.

At intervals the jars were taken to the balance and the weight of the container and its sample determined. This procedure was continued until a constant weight was reached indicating that the system had reached a point of equilibrium. The sample was then tested immediately or else kept under the same conditions until a later date when it was reweighed and then tested. If a sealed jar or desiccator was left out of the constant temperature box for any length of time water vapor condensed on the side of the jar and on the sample, and a check of the weight showed that the sample contained more moisture than was adsorbed under the regulated conditions. In some runs weighings were made every hour to determine the rate of adsorption. In these runs three jars were used at the same relative humidity so that the jars could be rotated and hourly readings taken without having to open any one jar more than once every three hours. This minimized the error due to a sample being out of the humid atmosphere during the time of weighing, and avoided disturbance of the air in the jar too frequently. In runs in which the same jar was opened and the same sample weighed every hour, the rate at which the moisture content increased was much slower than by the use of three jars. On the average a weighing could be made in less than thirty seconds by using the magnetic damper on the analytical balance. Checks of weights determined by this method with weights determined by the swing method indicated the same degree of accuracy.

2. Testing Procedure.

Testing on both the impact machine and the spark gap apparatus was based on the Bruceton Method which is usually referred to as the "Up and Down" or "Staircase Case" Method (6). This method is based upon the principle of concentrating the trials in the vicinity of the 50% point of explosion by raising or lowering the test statistic after each trial. In the case of an impact test, if an explosion occurs the drop height is decreased a fixed amount whereas if the trial results in a non-explosion, the height is increased and decreased as the test proceeds, thus concentrating the trials in the area where the true mean or 50% point is located. A greater reliability is achieved for a given number of trials by use of this method. The fifty percent point can

then be determined by plotting the results on probability paper or by the use of a formula devised for this purpose. The standard deviation can be estimated by taking the distance between the 95% point and the 5% point and dividing it by two times 1.645. The figure 1.645 is taken from statistical tables of the Cumulative Normal Distribution Function for a two-sided test with a level of significance of 0.90 (6). The change in height between trials should be approximately one standard deviation.

The modification of this general method used for testing in this project was patterned after that used by J. E. Sinclair (4). A modification was made in the starting point for the test. Each test was started at the 50% point determined from a dry sample of the substance being tested. The justification for such a starting point lies in the fact that the objective of the test was to detect any variation of the moist sample from that of a dry sample rather than to determine an accurate 50% point for the moist sample. The same method was used for tests conducted on the spark gap apparatus. In place of five centimeter changes in drop height, five volt changes on the primary of the coil of the transformer were used. Other than that the procedures for the tests were the same. The assumption was made that on any trial an explosion at a particular height would have been an explosion at any greater height, and that any non-explosion would have been a non-explosion at a lesser height. Each test consisted of from 20 to 25 trials. The 50% point was determined from a plot of the results on probability paper. An example of a completed form used for recording test results is shown in Figure 8.

A test on a dry sample was run during the course of each series of tests on a particular explosive or igniter on the spark gap apparatus. This established a firm basis for comparison with the succeeding or preceding tests on moist samples. About enough powder for five trials was removed from the humidified container at a time so as to lessen the time of exposure to the conditions in the room before being tested.

The squib was cleaned after every ten trials. It was found that black powder could not be ignited in a squib which was too clean or in one which was excessively coated with the residue of combustion. The first shot in a new squib with black powder had to be confined before it could be ignited. Attempts to fire black powder in a new squib with high voltage only resulted in the unignited powder being blown out of the squib. After one ignition had been attained the remainder occurred in a uniform manner at low voltage. Lead styphnate and the metallic mix could be initiated in any but a heavily coated squib. The procedure of scraping out the squib after every ten trials resulted in consistent results for all three substances.

Sensitivity Test Data Sheet

Lead Styphnate Containing 4.1% Moisture

Fifty Percent Point 21 volts.

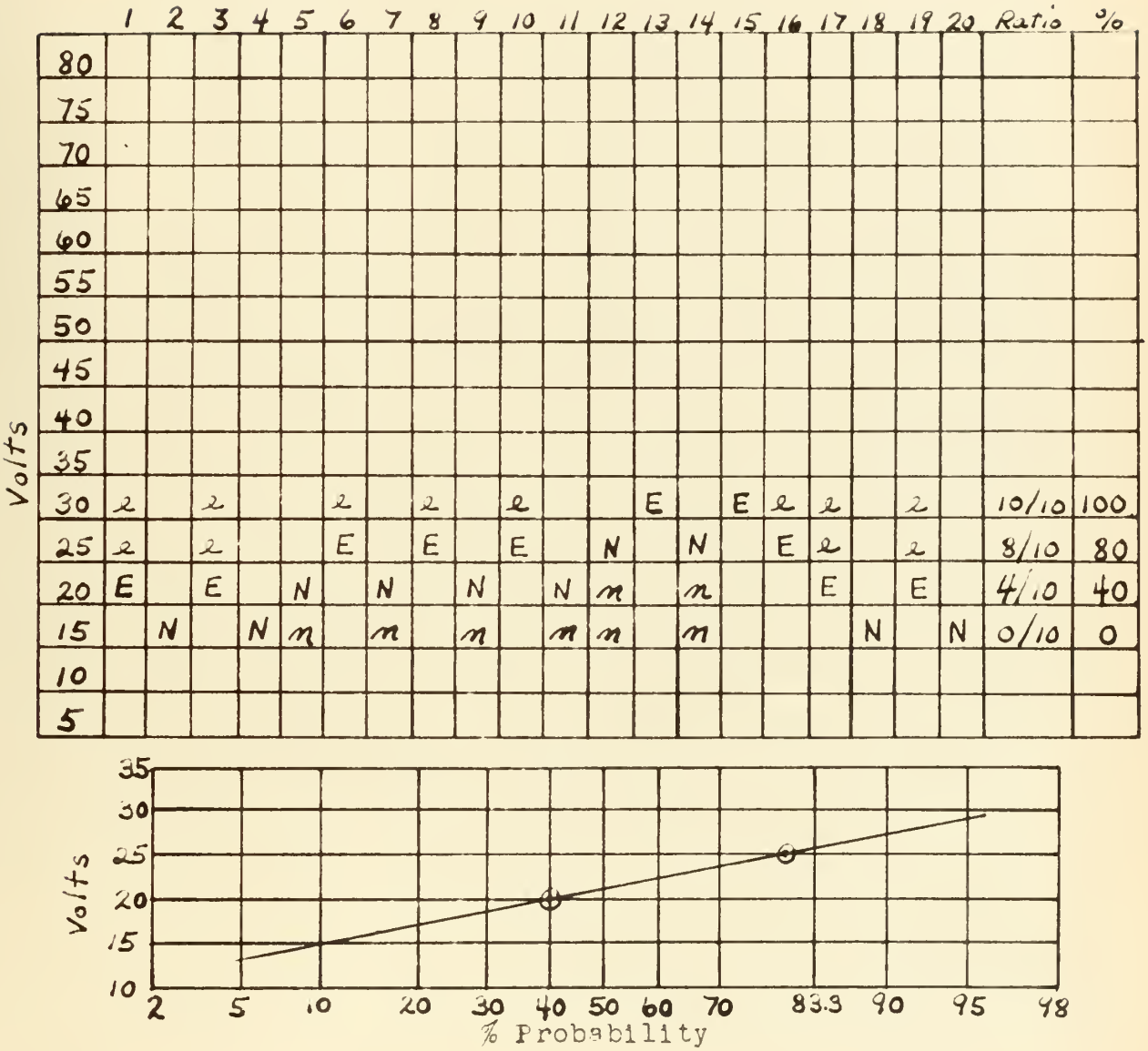


Fig. 8. Form Used For Recording Test Results.
Data is for a test on Lead Styphnate containing 4.1% Moisture.

EXPERIMENTAL RESULTS

BLACK POWDER

Black powder was not sensitive to water vapor at relative humidities up to 85%. Above 85% there was a rapid rise in the moisture content of the samples at equilibrium with increasing relative humidity. Figure 9 on page 22 shows the average percentage of adsorption over the range of relative humidities. There was visual evidence of a high moisture content at high humidities. At 93%, the particles adherred to the bottom of the container and to each other, and at 100% condensation occurred in large amounts. When the amount of absorption reached approximately 40%, droplets of water were evident. In a period of five days at 100% humidity, there was an increase in weight of 220%, and the sample had become an aqueous solution of potassium nitrate with particles of charcoal suspended throughout. When samples containing water were dried, the charcoal and potassium nitrate were separated, but remixing and then testing showed the same thermal sensitivity as before exposure.

Samples of black powder which had been exposed at 85% relative humidity and above showed a loss in weight as compared to the original weight of the dry powder before exposure. In the case of the 100% relative humidity samples, the white potassium nitrate could be seen where some of the recrystallization had occurred on the outside of the container as well as on adjacent containers in the desiccator. A photograph of this phenomenon is shown in Fig. 12. In five samples of varying weights dried with alumina powder in a desiccator after having absorbed water, the loss in weight was nearly identical. It was apparent that the loss in weight in these cases was a function of the size of the container. At 85% and at 93% there was a loss in weight, but it was not nearly as great as at 100%. In this case, the loss was dependent on the surface area and the time of exposure. A representative loss in weight for exposure for four days at 93% humidity is 0.5%. A lesser loss was observed at 85%.

The rate of adsorption by black powder is shown in Figure 10 on page 23 as a function of time up to nine hours. The adsorption at 30% humidity was so little and the time for adsorption so long that it was not plotted. At 100% humidity for a period of 24 hours the amount absorbed reached 75% while at 93% equilibrium was reached at 10% in about 20 hours.

As would be expected, the small amount of adsorption at lower relative humidities had little effect on the thermal sensitivity. It averaged about two volts increase over that of dry powder for a sample containing one percent moisture. With an absorption of 10% moisture, the voltage required was twice that required for a dry sample, and there was a slight lag between closing the firing key and the ignition of the powder. Since there was no timing device on the apparatus, this effect was not taken into consideration. This tends to indicate that the thermal sensitivity was affected even more than indicated. Those samples exposed at 100% humidity and therefore containing water, shorted out the squib and could not be ignited even with the maximum voltage of 3,600 volts across the spark gap. A plot of sensitivity vs humidity is shown in Fig. 11.

LEAD AZIDE

Lead azide was the least hygroscopic of the four substances investigated. At a constant temperature of 82 degrees F., the adsorption was only 0.8% at 100% relative humidity. Figure 9 on page 22 shows the percentage of moisture gained for the various relative humidities. During a run in which temperature varied between 65 and 105 degrees F. at approximately 80% relative humidity, the sample adsorbed nearly two percent moisture.

The rate of adsorption varied from less than two hours to reach equilibrium at 100% relative humidity to about 12 hours at 30%. A separate graph of the rate of adsorption for lead azide was not prepared. However, it was practically identical at the various humidities to that shown for lead styphnate in Figure 10. When referring to this graph, it should be borne in mind that the amount of adsorption for lead azide is only about one-fifty that for lead styphnate.

The results of tests for thermal sensitivity of lead azide on the spark gap apparatus proved to be inclusive. Approximately 100 shots were attempted, using samples exposed to the various humidities being used. Positive reactions were achieved on 29 of these trials. Of the 29 positive reactions, only six were detonations while the remaining 23 were ignitions or low order detonations. Each time an explosition occurred, it was followed by a group of non-explosions at successively higher voltage settings. This was apparently caused by damage to the squib due to the brisance of the explosion. Two or three explosions resulted in all the porcelain insulation being blown out of the squib and it is probable that each explosion resulted in changes in the spark gap distance. The majority of the ignitions and detonations occurred at voltage setting between 60 and 80 volts. It is interesting to note that two detonations were initiated at the relatively low voltage setting of 40 volts, lower than any of the ignitions and at a much lower energy level than over 60 shots which did not explode or ignite. This is another example of the unpredictability of explosives. Although the data were not very reliable, the 50% point of explosion/ignition for lead azide on the spark gap apparatus was in the vicinity of 70 volts for each of the samples regardless of the moisture content in the range of 0.1 to 0.8 percent.

The role of lead azide in the ammunition train makes its impact sensitivity of much greater importance than its thermal sensitivity. There was a decrease in impact sensitivity of about 10% on the impact machine for a sample with 0.8% moisture as compared to a dry sample. The sensitivity for a sample exposed at 30% was about the same as a dry sample, and the increase in drop height corresponding to the 50% point of explosion was nearly linear up to the average height required for a sample from a 100% relative humidity atmosphere. The graph of sensitivity as a function of relative humidity is shown in Fig. 11.

Zirconium Ignition Mixture

The pattern of the metallic ignition mix, with respect to its hygroscopicity and to the resulting effect on its thermal sensitivity, was very similar to that observed for black powder. The lowest

humidity at which adsorption was noted for this igniter was 50%, whereas a very slight amount of adsorption took place in black powder at 30%. At 85% it picked up only 0.3%, while black powder had a corresponding gain of about one percent. Graphs of both igniters are shown on Fig. 9. Above 90% the amount of adsorption increased rapidly from about three percent at 93% to over 40% with condensation at 100% relative humidity. Adsorption continued in saturated air until the presence of liquid water became noticeable when the moisture content reached about 40%. The nitrate compound, apparently placed in the metallic mixture as the oxidizer, dissolved in the water in the same manner as did the potassium nitrate in the black powder. A photograph of the recrystallization on the sides of the container is shown in Fig. 12. On drying the wet sample and remixing the compounds, the mixture once again had the same thermal sensitivity as a dry sample. No attempt was made to see just how much water would be collected at 100% relative humidity, but during a period of four days at this humidity a gain in weight of over 70% was observed.

The rate at which adsorption took place was also similar to the oorresponding rates for black powder which are shown in Fig. 10. In a saturated atmosphere the amount of moisture adsorbed at any particular time lagged slightly behind that of black powder, while at the lower humidities, each reached its equilibrium point in approximately the same length of time.

The thermal sensitivity of this metallic ignition mix was practically unaffected by the amount of moisture it had adsorbed at humidities of 85% and below. A moisture content of three percent increased the voltage required for the 50% point of ignition about 40% above that required for a dry sample. However, this represented an increase of only about five volts on the primary coil of the transformer. The wet samples which collected water as a result of being exposed to saturated air of course could not be ignited. Figure 11 shows the voltages required for the 50% point of ignition plotted with an abscissa of percentage relative humidity.

LEAD STYPHNATE

Lead styphnate was very sensitive to moisture over a wide range of humidities. The curve of moisture adsorbed shown in Fig. 9 shows a rapid rise from zero to 30% relative humidity, a more gradual rise on up to 70%, and only a slight increase from there to 100%. The solid portion of the curve on Fig. 9 was based on data obtained for exposure times of less than 24 hours. The curve for times of exposure in excess of 24 hours shows a slightly higher amount of adsorption over the range from 70% to 81% than at the higher humidities. This is shown by the dotted line on the curve for lead styphnate in Figure 9. This is not in agreement with the theory of adsorption and the explanations for this phenomenon is not apparent at this writing.

The rate of adsorption for lead styphnate is shown in Figure 10. The time to reach equilibrium at high vapor pressures was short, and the time increased with decreasing vapor pressure as was pointed out for lead azide.

Preparation of this explosive for use when starting with a few grams which had been under ethyl alcohol for a long period of time consisted merely of heating in a vacuum over for a sufficient length of time to drive off all the volatiles. Toward the end of the investigation attempts were made to use some of the compound which had been exposed to moisture previously. Three days in a desiccator with alumina powder was ineffective in removing the moisture. Three days in the vacuum oven did not completely dry the powder either. The procedure of soaking it in ethanol for one day followed by three days in the vacuum oven at 170 degrees F was found to be necessary to completely dry a sample which contained moisture.

The thermal sensitivity of lead styphnate was decreased to some extent by the presence of moisture. On the basis of 12 volts for the 50% point of explosion, it was found that twice that amount was required for a sample which contained four percent moisture. Samples

which had adsorbed slightly more than four percent required an average of 28 volts. One sample, which had been exposed for a prolonged period during which the temperature was not continuously regulated, gained 8.1% moisture. This sample could not be detonated in the spark gap apparatus. Instead of explosions, ignitions or low order detonation occurred. The 50% point for this sample was 50 volts, over four times the amount required for a dry sample. The voltages for the 50% point as a function of % relative humidity are shown on Figure 11.

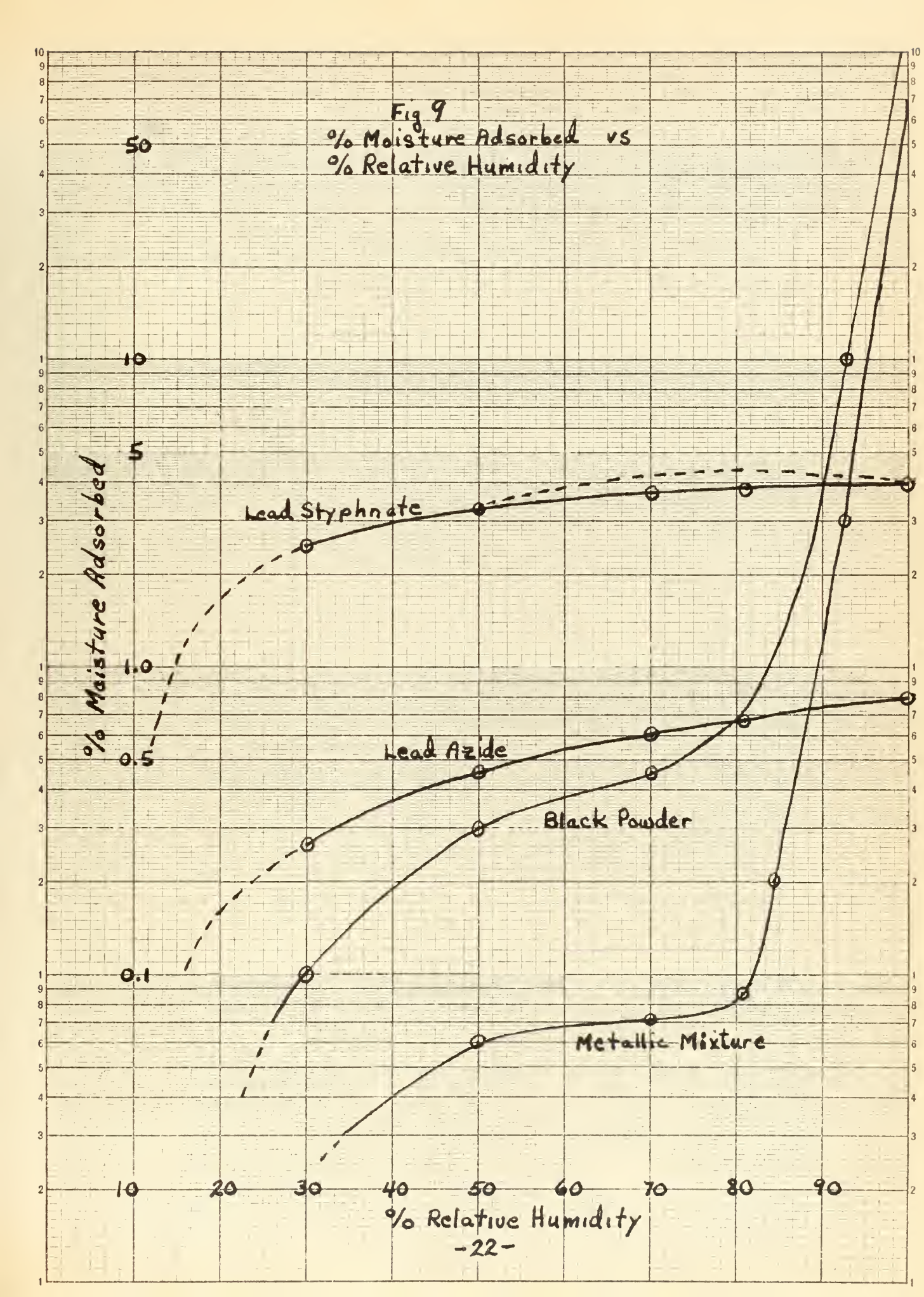
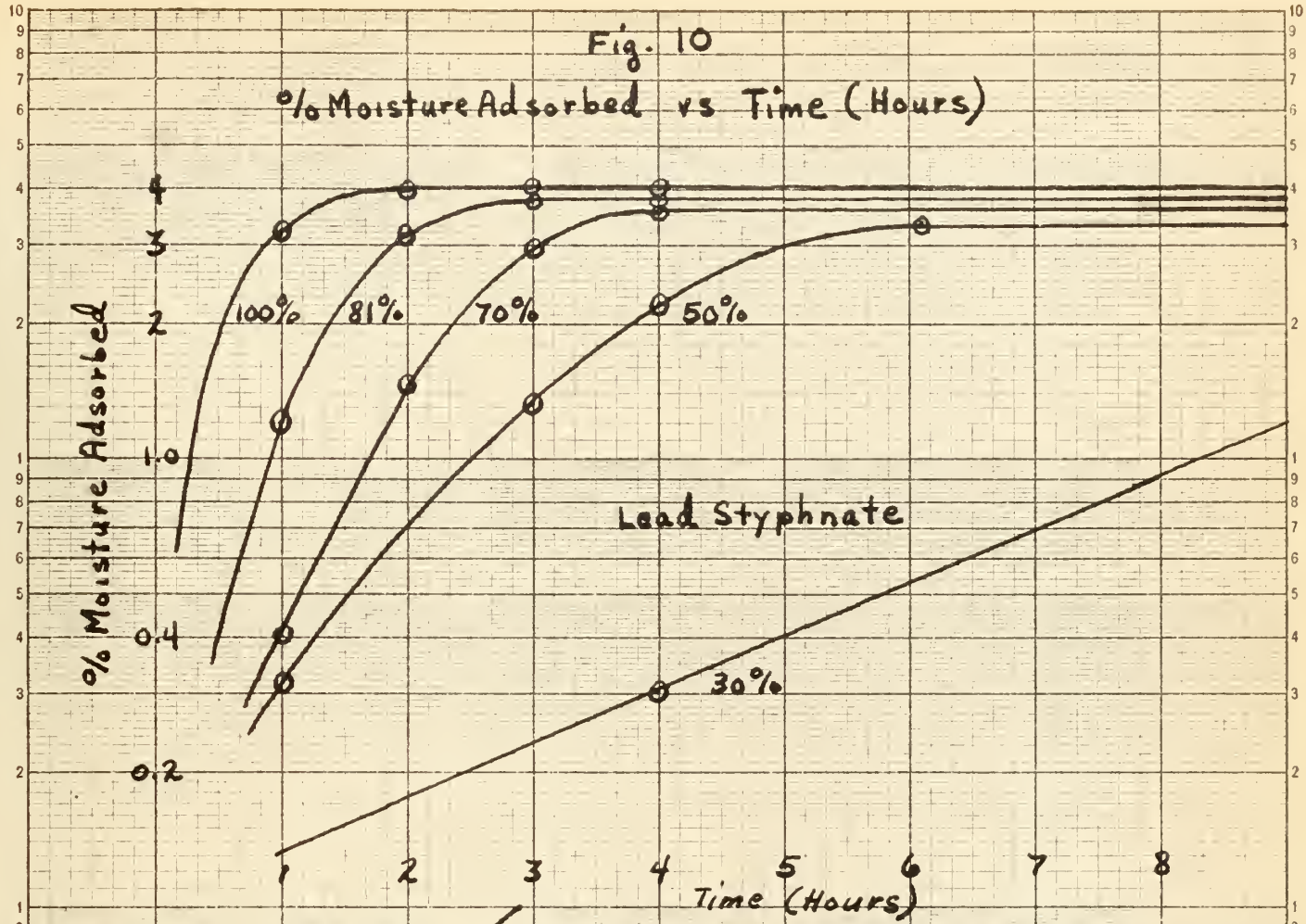
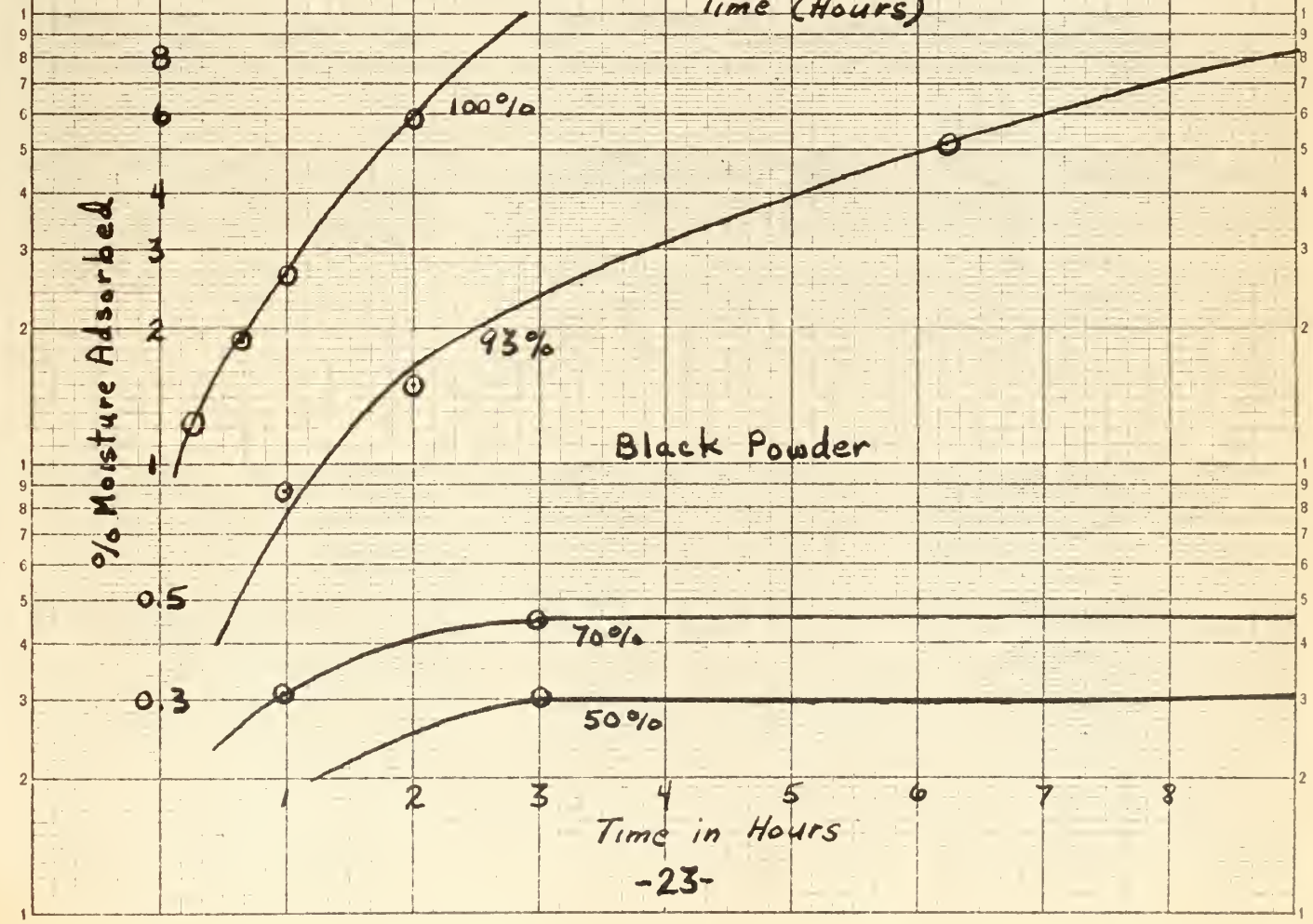


Fig 9
% Moisture Adsorbed vs
% Relative Humidity
50
10
5
1.0
0.5
0.1
% Moisture Adsorbed
Lead Styphnate
Lead Azide
Black Powder
Metallic Mixture
10
20
30
40
50
60
70
80
90
% Relative Humidity

Fig. 10

% Moisture Adsorbed vs Time (Hours)





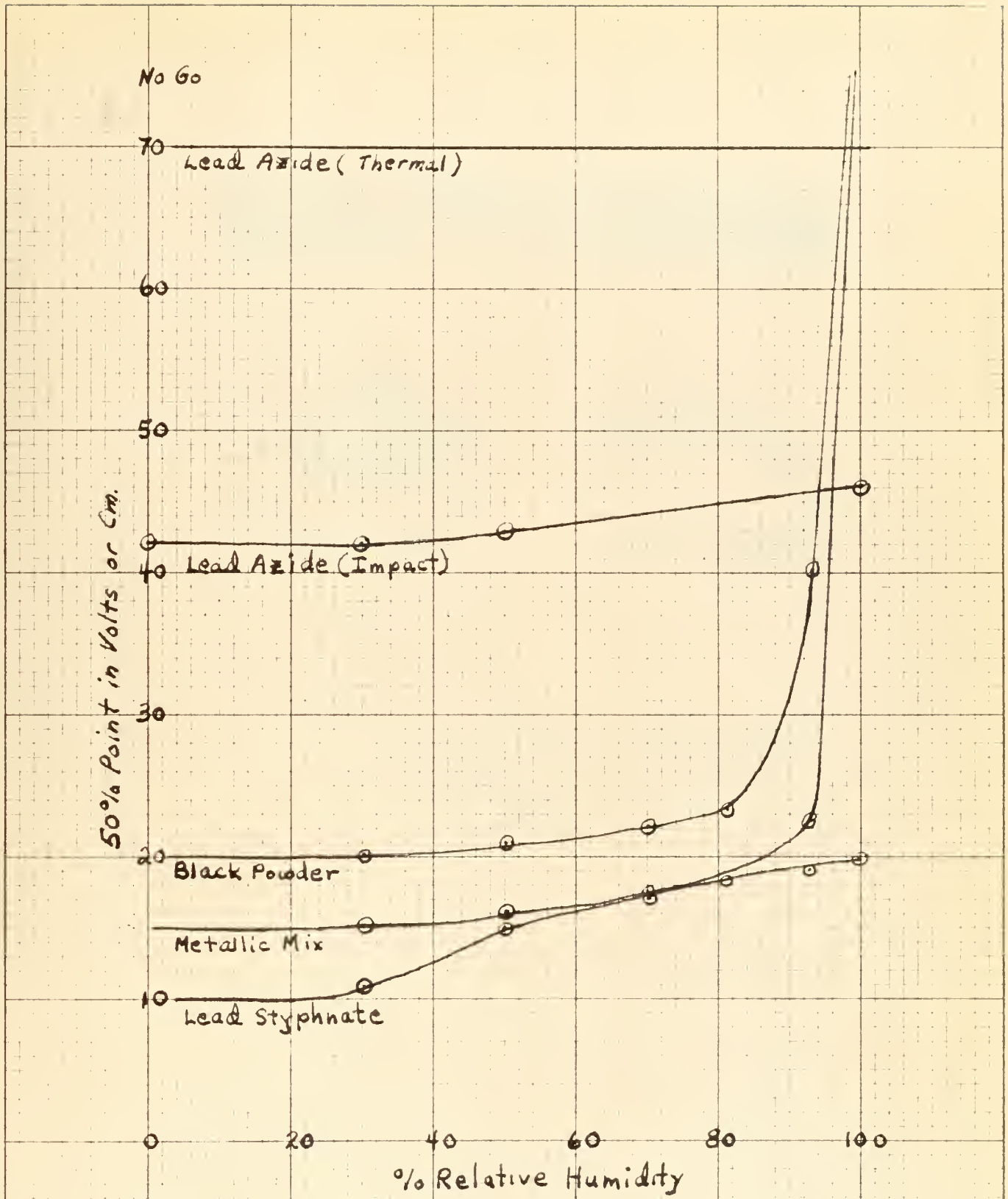


Fig. 11. 50% Point in Volts or Cm. vs % Relative Humidity

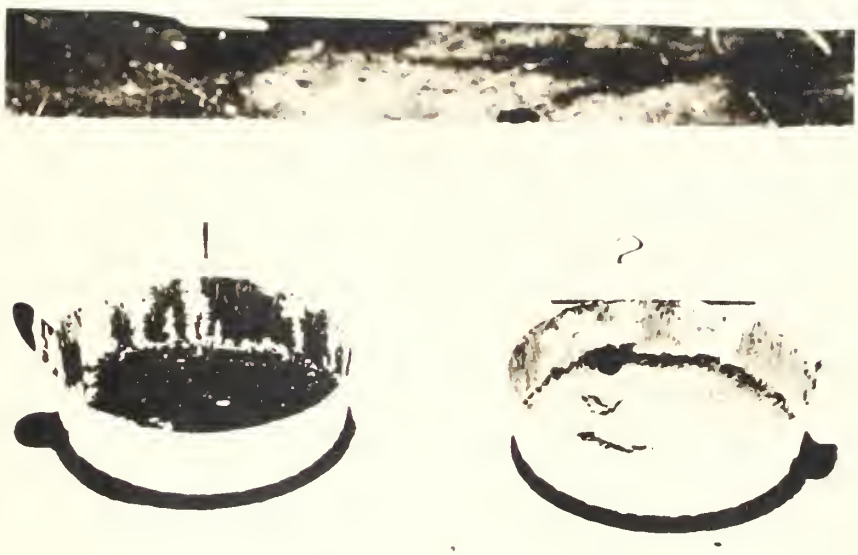


Fig. 12. Photographs showing the manner in which recrystallization occurs up the sides of the containers.
1. Black Powder
2. Metallic Ignition Mix

CONCLUSIONS

Lead azide is nearly non-hygroscopic when kept at a constant temperature of 82 deg. F. until equilibrium is reached. It will adsorb only about 0.8% moisture from an atmosphere saturated with water vapor. The effect of this amount of adsorption is to decrease its impact sensitivity about 10%. Under conditions of changing temperature and relative humidity, it is possible that the amount of adsorption will reach a value of approximately two percent with long periods of exposure. The presence of this amount of moisture decreases the impact sensitivity over 30%.

Black powder and the metallic ignition mixture are only slightly hygroscopic at relative humidities of 85% and less. Above 93% there is a rapid rise in the moisture content with time and increasing relative humidity,until at 100% an aqueous solution of the soluble salts in the mixture results. This can be explained by capillary condensation of the water vapor in the pores of the particles which dissolves the soluble salts present. The solution lowers the vapor pressure which results in further condensation until sufficient dilution has taken place to overcome this effect. A leaching of the soluble particles was also noted in black powder down to a relative humidity of 85%. The loss in weight is attributed to the soluble particles being carried out of the container by the departing water molecules. This phenomenon occurred very slowly and the loss increased with time and surface area exposed. No such loss was apparent in the metallic mixture when exposed at 93% for a period of four days, but during this time, black power had lost 0.5% of its original weight. A loss in weight of the metallic mixture was noted at 100% as shown in Fig. 12. Desorption of both igniters is very rapid when the relative humidity is lowered. Both black powder and the metallic ignition mixtures become useless as igniters when exposed at relative humidities slightly above 93% for periods of 24 hours or longer without subsequent drying.

Lead styphnate gained about four percent in weight due to moisture adsorption at the higher relative humidities. It was difficult to dry and required soaking in ethanol for a period of one day, followed by drying for at least three days in a vacuum oven at 170 deg. F. before separation of the moisture was assured. These factors tend to indicate that a chemical change had occurred in which the compound changed from the anhydrous to the monohydrate form. The Encyclopedia of Chemical Technology (7) states that it normally recrystallizes with one-half of a molecule of water of crystallization. The Condensed Chemical Dictionary (8) gives values for the specific gravity of both the anhydrous and the monohydrate of lead styphnate. A further check of the literature gave no additional information along this line. Lead styphnate which contains four percent moisture is only about one-half as sensitive as the dry form. Adsorption in addition to hydration is also possible with this compound. The presence of eight percent moisture made the lead salt of trinitroresorcinol unusable as an initiator.

A check was made on the effect of temperature on the amount of adsorption of the substances being investigated. It was found that there was less adsorption at 96 deg. F. than at 82 deg. F., and more adsorption at 38 deg. F. than at 82 deg. F. This agrees with the theory that adsorption increases with decreasing temperature.

The curves of percentage moisture adsorbed, versus relative humidity shown for all four substances in Fig. 9, have the same general shape as those shown in reference (1) for the various types of adsorption isotherms. The curve for black powder and the metallic mixture agree with a typical curve for monomolecular adsorption with capillary condensation at higher pressures, lead styphnate agrees with the Langmuir curve in which the surface is completely covered or saturated, and lead azide agrees with the Freundlich curve in which the surface is only partially covered. The curves for lead azide and styphnate are readily solved by the Freundlich and Langmuir equations when the corresponding partial pressure of the water vapor is substituted for relative humidity.

The graphical solution of the Freundlich Equation is shown in Fig. 13, and for the Langmuir Equation in Fig. 14. When log y is plotted as a function of log p_s, the intercept at p_s equal zero gives the value of k, while the slope gives the value of z for the Freundlich Equation. An explanation of the symbols is contained on page v. When p_s/y is plotted as a function of p_s, the intercept gives the reciprocal of ab, and the slope gives the reciprocal of b for the Langmuir Equation. Using the constants computed from the graphs, the percentage of moisture which will be adsorbed at the various partial pressures can be calculated by the following equations:

Lead Styphnate:

$$y = 1.23(p_s)^{0.35}$$

$$y = \frac{(0.092)(5.55)(p_s)}{1 + [(0.092)(p_s)]}$$

Lead Azide:

$$y = 0.038(p_s)^{0.91}$$

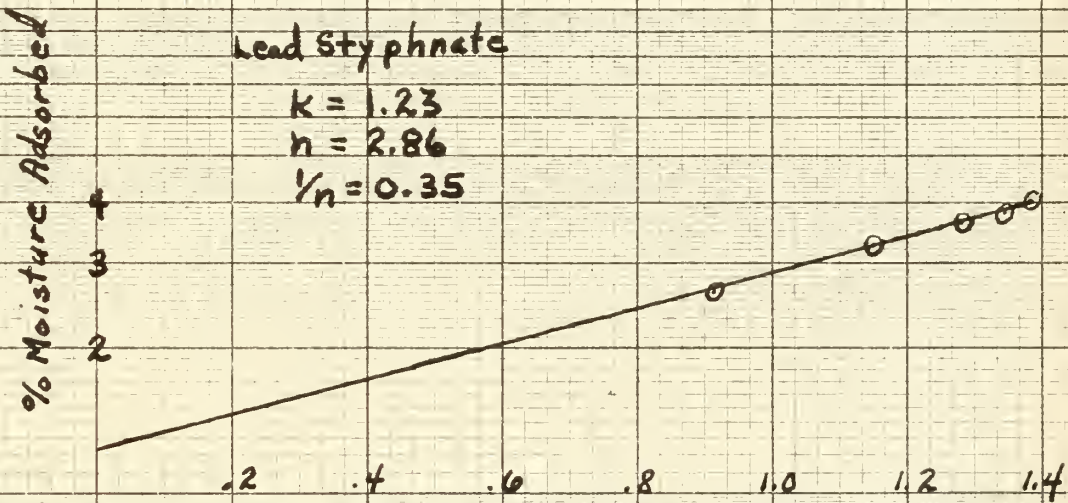
$$y = \frac{(0.008)(4.38)(p_s)}{1 + [(0.008)(p_s)]}$$

The Langmuir Equation agrees more closely with the data over the entire range of the partial pressures. This is to be expected because of the purely empirical basis of the Freundlich Equation as compared to the theoretical basis for the Langmuir Equation. No solution is offered for the Patrick Equation, since the process used during the experiment was both constant temperature and constant total pressure, and the solution would therefore be similar to the Freundlich Equation.

Fig 13

Log % Moisture Adsorbed vs Log Ps (mm Hg.)

Graphical Solution of Freundlich Eqn



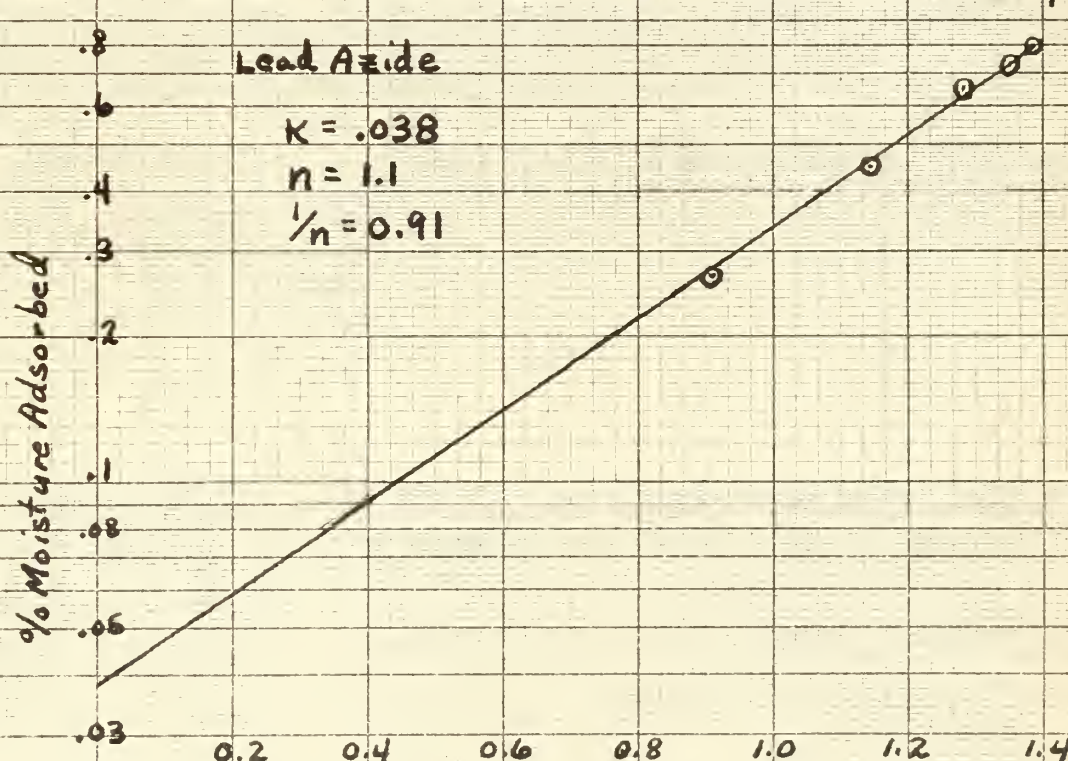


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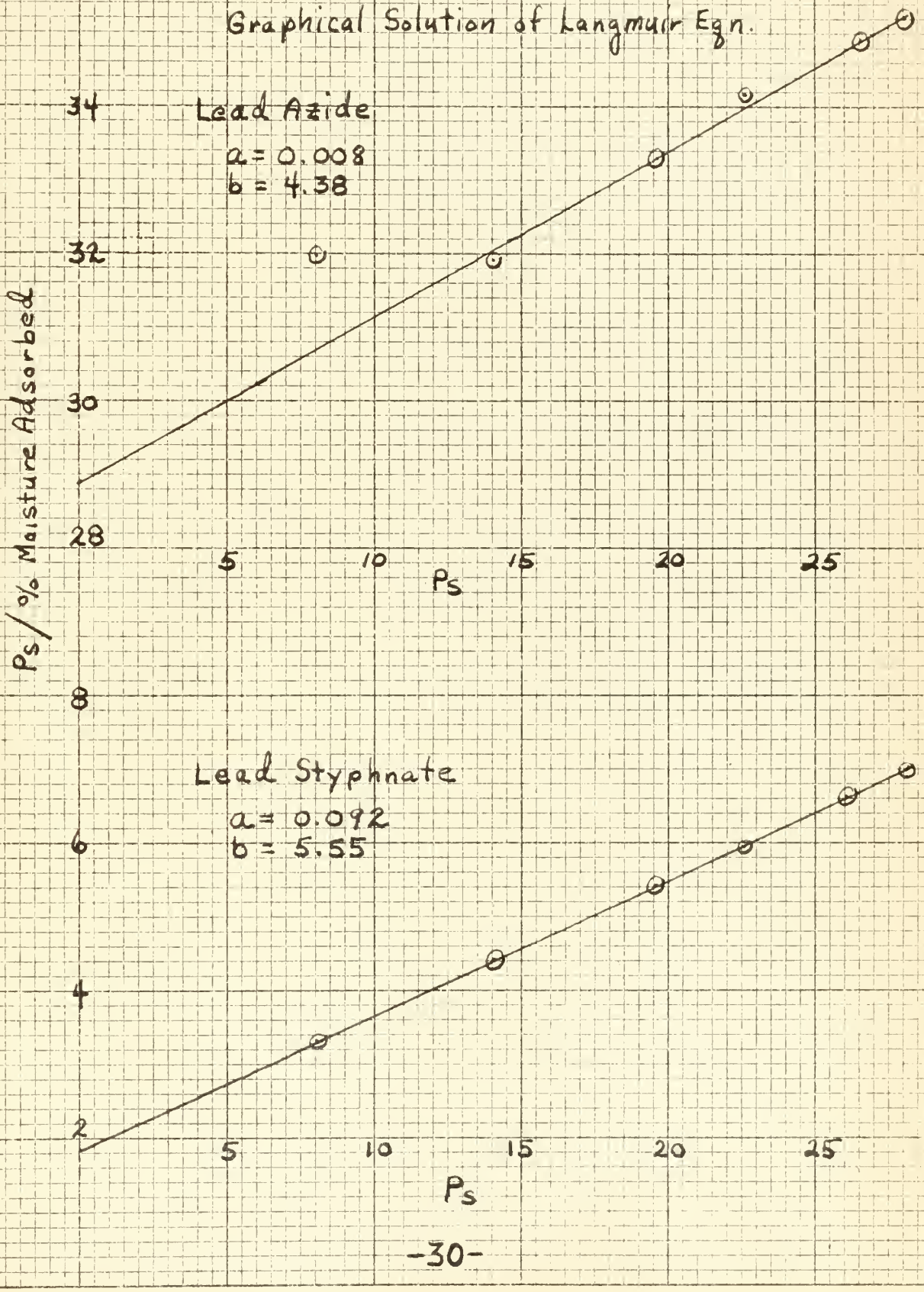
Fig. 14

P_s/% Moisture Adsorbed

vs

P_s

Graphical Solution of Langmuir Eqn.



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